Conductivity and Viscosity of Solutions of Rubidium Salts in Mixtures of Acetone and Water

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

HORATIO HUGHES

JUNE, 1913

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CONDUCTIVITY AND VICOSITY OF SOLUTIONS OF RUBIDIUM SALTS IN MIXTURES OF ACETONE AND WATER.

Introduction

During the past twelve years work has been in progress continuously in this laboratory on the conductivity and viscosity of solution of salts in pure and mixed solvents, in connection with the nature of solution. A number of papers on this subject have already been published.

Jones and Lindsay[1] explained the minima in the conductivity curves in mixtures of alcohol and water, as due to each associated solvent breaking down the association of the other associated solvent.

Jones and Murray[2] showed experimentally that when one associated solvent is mixed with another associated solvent, each diminishes the association of the other.

Jones and Carroll[3] showed that the change in viscosity when alcohol and water are mixed, must be taken into account in dealing with the conductivities in mixtures of such solvents.

Jones and Bassett[4] studied the ionic velocities of the ions of silver nitrate in pure and mixed solvents.

Jones and Bingham[5] not only measured conductivities in but viscosities of mixed solvents and of solutions in them.

Jones and Rouiller[6] studied the migration velocities of the

[1] Amer. Chem. Journ. 28, 329 (1902); Zeit. f. physik. Chem. 56, 129 (1906).

[2] Amer. Chem. Journ., 30, 139 (1903).

[3] *Ibid.*, 32, 521 (1904); Zeit. f. physik. Chem., 56, 150 (1906).

[4] Amer. Chem. Journ., 32, 409 (1904).

[5] Amer. Chem. Journ., 34, 481 (1905); Zeit. f. physik. Chem., 57, 193 (1906).

[6] Amer. Chem. Journ., 36, 427 (1906).

ions of silver nitrate in mixtures of acetone and methyl alcohol using the migration of velocity apparatus designed by Jones.[1]

Jones and McMaster[2] found maxima in the conductivity curves in mixtures of acetone and the alcohols. These they explain in terms of the solvate theory of solution proposed by Jones.

They also found negative temperature coefficients of conductivity for cobalt chloride in a certain mixture of acetone and ethyl alcohol. These were explained.

Jones and Veazey[3] obtained some of the most interesting results in the early stages of this work. When alcohol and water are mixed there is a marked increase in viscosity. This was shown to be due to each associated solvent breaking down the association of the other; a larger number of smaller particles exerting greater friction when moving over one another, than a smaller number of larger particles. This explanation is in keeping with the fact that the most strongly associated liquids show, on mixing, the greatest increase in viscosity.

Jones and Veazey also explained the fact that certain salts *lower the viscosity of water.* These are salts of potassium, rubidium and cæsium. These elements have the largest atomic volumes; their atomic volumes being much greater than the molecular volume of water. When these large ions are mixed with water they diminish the frictional surfaces in contact with one another, and, consequently, the viscosity which measures the friction of the molecules as they move over one another. The effect of a dissolved salt on the viscosity of water was shown to be dependent on the atomic volumes of its constituents, and this was shown to hold throughout the entire Periodic System.

The investigations of Jones and his co-workers, thus far re-

[1] Amer. Chem. Journ., 32, 409 (1904).

[2] *Ibid.*, 36, 325 (1906); Zeit. f. physik. Chem., 57, 257 (1906).

[3] Amer. Chem. Journ., 37, 405 (1907); Zeit. f. physik. Chem. 57, 193 (1907); 62, 44 (1908).

ferred to, have been published by the Carnegie Institution of Washington as monograph No. 80.

Jones and Mahin [1] studied the conductivities and viscosities of solutions of tetraethylammonium iodide in pure and mixed solvents. They also studied the conductivities and viscosities of solutions of lithium nitrate in ternary mixtures of certain solvents.

Jones and Kreider [2] measured the dissociation of certain electrolytes in the alcohols by the conductivity method. They found the following relation:

$$\frac{\mu_\infty \text{ in methyl alcohol}}{\mu_\infty \text{ in ethyl alcohol}} = \text{constant.}$$

The value of this constant for binary electrolytes is 2.37; for ternary electrolytes is 3.68.

In their later work they show that the above relation holds for salts that are solvated to approximately the same extent.

Schmidt and Jones [3] extended these investigations to glycerol as a solvent. The object was to work with a solvent with very large viscosity and see what relations would manifest themselves. The temperature co-efficients of conductivity in glycerol as the solvent, were found to be enormous.

Guy and Jones [4] extended the work of Schmidt and Jones in glycerol as the solvent; working from 25° to 75°. They also worked in mixtures of glycerol with water and the alcohols. Those salts which, in general, have the greatest solvating power, have the largest temperature coefficients of conductivity in glycerol; and these are greater in the more dilute solutions. This is strictly analogous to what has been pointed out for aqueous solutions, by Jones,[5] from the work of Jones and West.[6]

[1] Zeit. f. physik. Chem., 62, 44 (1908); Amer. Chem. Journ., 41, 433 (1909).

[2] *Ibid.*, 45, 282 (1911); 46, 574 (1911).

[3] Amer. Chem. Journ., 42, 37 (1909).

[4] *Ibid.*, 46, 131 (1911).

[5] Amer. Chem. Journ., 35, 445 (1906)).

[6] *Ibid.*, 34, 357 (1905).

Probably the most important point established by the work of Guy and Jones is that while most salts raise the viscosity of glycerol, *salts of rubidium and ammonium lower the viscosity of glycerol.* This is exactly analogous to what was found for aqueous solutions. There, salts of potassium, rubidium and cæsium lowered the viscosity of water, and the explanation offered by Jones and Veazey has already been referred to. The same explanation holds in glycerol as the solvent.

Davis and Jones [1] extended the work still further in glycerol as a solvent. They studied especially the conductivities and viscosities of glycerol solutions of ammonium and rubidium salts. Salts of rubidium lower very greatly the viscosity of glycerol. Ammonium salts lower the viscosity of this solvent much less than salts of rubidium. The lowering of the viscosity is less the higher the temperature and the greater the dilution. These facts are all in keeping with the theory of Jones and Veazey to account for such phenomena. The work of Jones with Mahin, Kreider, Schmidt, Guy and Davis; also with Stine [2] and Pearce,[3] is now in press as a whole, and will soon be published as Monograph No. 180 by the Carnegie Institution of Washington.

The work in nonaqueous and mixed solvents especially including acetone and formamide, is now in progress in this laboratory. We expect to continue such work for many years to come, studying a much larger number of nonaqueous solvents, and a much larger number of substances dissolved in them.

All previous work in this laboratory with acetone as a solvent shows that it has exceptional properties. Measurements of both conductivity and fluidity have usually given results that are abnormal in terms of other solvents. For this reason it was chosen as a solvent in this investigation. It was hoped that with such a solvent, the property possessed by rubidium salts of forming

[1] Zeit. f. physik. Chem. 81, 68 (1912).
[2] Amer. Chem. Journ., 39, 313 (1908).
[3] *Ibid.*, 38, 683 (1907).

solutions having a lower viscosity than that of the solvent might throw some additional light upon the phenomena presented by solution.

Only mixtures of acetone and water have been used, because in pure acetone the rubidium salts studied are not sufficiently soluble to affect the fluidity to a measurable extent.

Experimental

Conductivity Apparatus

Bridge.—The conductivity measurements were made by means of a slide wire bridge which is about five meters long, the balance being detected by a telephone receiver. The bridge and rheostat were made and standardized by Leeds, Northrup and Co. of Philadelphia, Pa.; and the rheostat was compared with one which had been recently standardized by the United States Bureau of Standards.

A double system of wiring was used between the rheostat, slide wire and cells, so that by means of a double arm double throw switch the arms of the bridge could be interchanged. In this way the resistance a of the first portion of the slide wire was read and then b $(= 1000 - a)$ for comparison. The circuit was opened and closed by an ordinary telegraph key whose resistance was made of negligible quantity by connecting the frame to the lever by a short spring of large copper wire.

The wire used throughout was number 12 gauge and the cells containing the solutions were connected with the rest of the bridge by a large flexible cable of copper having a negligible resistance. All connections were soldered, and the various portions of the apparatus were tested for any appreciable resistance. The two halves of the double system for reading a and b were carefully compared and b was found not to differ from 1000-a by any appreciable quantity, except for resistances

smaller than any used in this investigation—that is below 10 ohms.

Cells.—The conductivity cells were of three forms. For the most concentrated solutions two U cells with adjustable electrodes were employed having constants of about 15 000. and 30 000. The most dilute solutions, and the solvents, were measured in cells with cylindrical electrodes of the type described by Jones and Schmidt,[1] and by Jones and Kreider,[2] and with constants ranging from 2.9 to 4.3. The intermediate dilutions, that is from N/10 to N/400 solutions, were measured in cells of the plate type described by Jones and Bingham.[3]

Constant temperature.—The constant temperature baths were the usual form with double walls insulated by asbestos, heated by gas from beneath, and cooled by spiral coils of copper tubing placed close to the bottom. Water could be passed through these coils at a uniform rate by means of the head from a two and one-half metre stand-pipe. This facilitated temperature regulation at or below room temperature. An auxiliary coil of copper tubing immersed in an ice bath was also introduced into the cooling system by means of brass unions, whenever the average temperature of the tap water was too high to give good regulation. By means of electrically operated gas valves, temperatures were kept constant, over any desired length of time, to within 0°.01.

Volumetric apparatus.—All flasks were carefully calibrated to hold aliquot parts of the true litre at 20°, and solutions were brought to within 0°.1 of this temperature before being diluted to the mark.

Solvents

Water.—The water was purified by the method of Jones and Mackay [4] as modified by Schmidt, and has a mean specific conductivity of 1.5×10^{-6} at 25°.

[1] Amer. Chem. Journ., **42**, 39 (1909). [2] *Ibid.*, **45**, 282 (1911).
[3] *Ibid.*, **34**, 481 (1905). [4] Amer. Chem. Journ., **17**, 83 (1895).

Acetone.—Kahlbaum's so-called pure acetone was allowed to stand for several days over calcium chloride, and distilled two or three times. No difficulty was experienced in obtaining a product of approximately the same conductivity as the water used in this work. Solutions were made up as quickly as possible after distilling the acetone, which was always kept in a dark place.

Mixtures of Acetone and Water.—The mixtures used as solvents were made by diluting a given volume of acetone to a definite volume with water at 20°. For convenience, the number of cubic centimetres of acetone diluted to one hundred cubic centimetres was indicated as the "percentage" of acetone in the solvent. A very considerable contraction takes place when acetone and water are mixed, so that the figures used to designate the mixture are, of course, not true percentages, either by weight or volume. The true percentage, however, is of no consequence as long as the mixture is thus defined. Actually, the mixture of 500^{cc} acetone diluted to one litre at 20° contains about 42% by weight of acetone and the mixture of 250^{cc} of acetone diluted to one litre contains approximately 20% by weight of acetone.

Solutions

Solutions of one tenth normal and all greater concentrations were made by dissolving the requisite weight of salt. The N/50 and N/100 solutions were made from the N/10 by dilution; and the N/200 and N/400, respectively, were made from these. The N/800 and N/1600 concentration were prepared in the same manner from the N/200 and N/400. The last two concentrations were thus made in three dilutions from the N/10 concentration. Upon the basis of a probable percentage deviation of 0.10% in the original weight of salt, and in the measurement of the solvent in the flask, and of 0.40% in the measurements from the burettes, the probable errors in the value of V in these greatest dilutions is about 0.70%. The

probable error in the other dilutions is, of course, much less than this, being within 0.14% in the case of the N 10 and all greater concentrations.

All solutions were made up at 20°. No correction for changed normality at higher temperatures has been applied to the values obtained for molecular conductivity. Rise in temperature, of course, diminishes the normality of a solution. This effect is accompanied by an increase in molecular conductivity, which is complex. While this increase in conductivity due to temperature is of the same order of magnitude as that produced by the same lowering of normality caused by diluting with more of the solvent, the two effects bear no known relation to each other.

Salts

The rubidium salts used in this work were Kahlbaum's purest products. They were recrystallized two or three times from conductivity water, precipitated and washed with alcohol, and dried at 120° to 135° according to the nature of the salt. The iodide was pure white after drying, and the more concentrated solutions were only slightly coloured after standing several days.

Procedure

Conductivity Measurements

The values of the molecular conductivity μ, are computed from the relation $\mu = K\frac{va}{wb}$ where v is the number of litres of solvent which contains a gram-molecular weight of the salt; w, the resistance in ohms; a b the ratio from the Wheatstone bridge; and K the cell constant.

The cell constants were determined with solutions of potassium chloride of N 50, N 500, and N 200 concentrations. The value taken for the molecular conductivity of the N 50 solution was that given by Ostwald, namely, 129.7 reciprocal

Siemens units at 25°. Three resistances were used in the measurement of each solution.

It should be pointed out that the fact that w is measured in ohms is not incongruous with the use of reciprocal Siemens units in the result, the factor 1/1.063 being included in the cell constants obtained. To convert the results given in the tables to reciprocal ohms, it is only necessary to multiply by 1.063.

The calculation of data was facilitated by the use of tables of values of $\frac{a}{b} / \frac{1}{w}$. By use of notation by powers of 10, twenty values of $\frac{1}{w}$ were sufficient for the preparation of these tables which were readily computed with a calculating machine. Not only does the use of such tables save considerable time in computation, but in their preparation, the chances of mistakes are eliminated by methods which do not obtain when the values are independently computed. The tables used in this work gave all Wheatstone bridge ratios from 400/600 to 600/400 by millimetres with interpola to tenths of millimetres.

The greatest error in the measurements of the components K, v, a, b, of the molecular conductivity, μ_v, occurs in the determination of the cell constants of the plate cells. This is subject to considerable variation and it was necessary to make frequent determinations of these values. Under average conditions the precision of μ_v is from 0.5 to 1.0%.

Temperature Coefficients.—The temperature coefficient in conductivity units is the increase in conductivity for each degree rise in temperature; that is:—

$$\text{Temp. coeff.} = \frac{\mu_{t_2} - \mu_{t_1}}{t_2 - t_1}$$

the temperatures compared always differing from each other by ten degrees. The temperature coefficients in per cent is the above quantity divided by the conductivity at the lower temperature, and multiplied by one hundred; *e. g.*:—

$$\%\ \text{coefficient} = \frac{\mu_{35°} - \mu_{25°}}{10} \cdot \frac{100}{\mu_{25°}}$$

Table I—Molecular Conductivity Rubidium Iodide in "75 per cent." Acetone

V	15°	25°	35°	45°
1	36.2	43.0	50.6	57.6
4/3	37.1	44.1	52.0	59.8
2	38.8	46.4	53.8	61.5
4	42.7	51.3	59.7	68.5
10	....	58.0	68.2	78.7
50	....	67.9	80.8	93.7
100	58.7	71.8	85.7	99.5
200	60.4	74.3	87.6	102.8
400	62.5	76.3	91.2	107.3
800	64.2	78.5	94.1	119.6
1600	65.2	80.1	95.3	111.4

Table II—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
1	0.68	0.75	0.71	1.88	1.75	1.40
4/3	0.70	0.69	0.78	1.89	1.56	1.50
2	0.75	0.74	0.73	1.93	1.63	1.36
4	0.87	0.84	0.88	2.03	1.67	1.47
10		0.93	1.05		1.61	1.53
50		1.30	1.29		1.92	1.60
100	1.38	1.39	1.38	2.37	1.93	1.61
200	1.39	1.33	1.52	2.31	1.79	1.78
400	1.38	1.49	1.61	2.21	1.95	1.77
800	1.43	1.55	1.55	2.23	1.95	1.67
1600	1.49	1.52	1.61	2.29	1.90	1.69

Table III—Molecular Conductivity Rubidium Iodide in "62.5 per cent." Acetone.

V	15°	25°	35°	45°
2	42.8	53.0	63.3	74.2
10	48.6	60.7	73.3	86.7
200	57.5	72.7	89.1	106.5

Table IV—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.01	1.13	1.09	2.37	2.13	1.73
10	1.23	1.26	1.34	2.52	2.08	1.82
200	1.52	1.65	1.74	2.64	2.27	1.95

Table V—Molecular Conductivity Rubidium Iodide in "50 per cent." Acetone.

V	15°	25°	35°	45°
1	46.5	57.4	68.6	81.0
4/3	46.7	58.1	69.8	82.9
2	47.2	58.8	71.0	83.9
4	49.0	62.0	76.0	91.8
10	51.5	65.3	80.3	95.2
50	55.5	71.0	87.7	105.7
100	56.6	72.2	89.7	108.8
200	58.3	74.9	92.8	112.3
400	59.0	75.8	94.0	114.1
800	60.2	77.7	95.9	116.5
1600	62.5	78.8	96.9	120.5

Table VI—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
1	1.087	1.124	1.236	2.34	1.96	1.80
4/3	0.940	1.169	1.314	2.02	2.01	1.89
2	1.16	1.22	1.29	2.45	2.08	1.82
4	1.301	1.40	1.575	2.68	2.26	2.07
10	1.379	1.502	1.49	2.68	2.33	1.86
50	1.55	1.67	1.80	2.79	2.35	2.05
100	1.56	1.75	1.91	2.76	2.42	2.13
200	1.56	1.79	1.95	2.68	2.39	2.10
400	1.68	1.82	2.01	2.85	2.40	2.14
800	1.75	1.82	2.06	2.91	2.35	2.15
1600	1.63	1.81	2.36	2.61	2.30	2.28

Table VII—Molecular Conductivity Rubidium Iodide in "37.5 per cent." Acetone.

V	15°	25°	35°	45°
2	42.8	53.0	63.3	74.2
10	48.6	60.7	73.3	86.7
200	57.5	72.7	89.1	106.5

Table VIII—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.41	1.49	1.59	2.62	2.19	1.92
10	1.66	1.66	1.77	2.95	2.28	1.99
200	1.82	1.97	2.13	2.86	2.41	2.09

Table IX—Molecular Conductivity Rubidium Iodide in "25 per cent." Acetone.

V	15°	25°	35°	45°
1	62.7	77.3	92.5	108.5
4/3	63.0	77.9	94.1	110.6
2	63.0	78.9	95.7	113.8
4	63.9	80.4	98.7	117.3
10	65.1	83.2	101.8	121.6
50	70.8	90.2	111.0	133.4
100	72.0	91.7	113.1	135.9
200	74.2	94.5	117.1	139.9
400	74.0	94.1	116.8	140.1
800	75.1	95.6	118.5	145.2
1600	75.8	96.4	118.3	141.5

Table X—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
1	1.45	1.52	1.61	2.32	1.97	1.74
4/3	1.49	1.62	1.65	2.36	2.09	1.75
2	1.59	1.68	1.81	2.52	2.12	1.89
4	1.65	1.84	1.85	2.58	2.28	1.88
10	1.81	1.86	1.98	2.78	2.24	1.94
50	1.94	2.08	2.24	2.74	2.31	2.01
100	1.97	2.14	2.28	2.74	2.34	2.02
200	2.03	2.26	2.28	2.74	2.39	1.95
400	2.01	2.27	2.33	2.72	2.42	2.00
800	2.05	2.29	2.67	2.73	2.40	2.25
1600	2.06	2.19	2.32	2.72	2.28	1.96

Table XI—Molecular Conductivity Rubidium Iodide in "12.5 per cent." Acetone.

V	15°	25°	35°	45°
2	76.2	94.2	112.5	131.6
10	80.6	100.4	121.4	144.0
200	89.9	113.4	137.7	163.1

Table XII—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.79	1.83	1.92	2.35	1.94	1.71
10	1.98	2.09	2.26	2.43	2.01	1.86
200	2.35	2.43	2.54	2.62	2.14	1.84

Table XIII—Molecular Conductivity Rubidium Bromide in "75 per cent." Acetone.

V	15°	25°	35°	45°
2	28.2	33.5	38.8	43.9
4	32.5	39.1	45.7	52.6
10	39.1	47.6	55.9	64.7
50	48.7	59.6	71.0	82.8
100	52.3	64.2	76.8	89.5
200	55.1	68.1	81.6	95.1
400	58.4	71.8	85.8	100.9
800	61.2	75.7	90.8	106.7
1600	65.9	81.3	97.8	114.9

Table XIV—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	0.529	0.53	0.52	1.88	1.58	1.34
4	0.655	0.66	0.68	2.02	1.69	1.49
10	0.845	0.83	0.88	2.16	1.74	1.57
50	1.09	1.14	1.18	2.25	1.91	1.66
100	1.19	1.26	1.27	2.28	1.96	1.65
200	1.30	1.35	1.35	2.36	1.98	1.66
400	1.34	1.40	1.51	2.30	1.95	1.76
800	1.45	1.51	1.59	2.37	1.99	1.76
1600	1.54	1.65	1.71	2.34	2.03	1.75

Table XV—Molecular Conductivity Rubidium Bromide in "62.5 per cent." Acetone.

V	15°	25°	35°	45°
2	36.2	44.2	52.7	61.5
10	43.5	53.9	63.8	74.2
200	56.5	72.7	87.1	103.9

Table XVI—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	0.80	0.84	0.88	2.18	1.90	1.67
100	1.04	0.99	1.04	2.39	1.84	1.63
200	1.62	1.44	1.68	2.87	1.98	1.93

Table XVII—Molecular Conductivity Rubidium Bromide in "50 per cent." Acetone.

V	15°	25°	35°	45°
1	40.9	50.5	60.6	71.3
2	43.3	54.2	65.7	77.8
4	45.8	57.9	70.6	84.7
10	47.8	59.8	72.5	84.8
50	54.6	69.8	86.3	103.0
100	56.6	72.4	89.9	107.9
200	57.5	73.8	91.5	110.0
400	59.3	76.1	94.5	113.3
800	60.7	78.1	97.4	117.2
1600	61.6	79.2	98.5	118.4

Table XVIII—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
1	0.956	1.01	1.07	2.34	2.01	1.76
2	1.09	1.15	1.21	2.51	2.12	1.82
4	1.21	1.27	1.41	2.64	2.19	2.00
10	1.20	1.27	1.23	2.51	2.13	1.70
50	1.52	1.65	1.67	2.78	2.37	1.94
100	1.58	1.75	1.80	2.80	2.42	2.00
200	1.63	1.77	1.85	2.84	2.40	2.02
400	1.68	1.84	1.88	2.83	2.42	1.99
800	1.74	1.93	1.98	2.87	2.47	2.03
1600	1.76	1.93	1.99	2.86	2.44	2.02

Table XIX—Molecular Conductivity Rubidium Bromide in "37.5 per cent." Acetone.

V	15°	25°	35°	45°
2	51.1	64.2	78.4	93.4
10	54.3	67.7	82.2	96.5
200	64.8	83.8	104.0	125.0

Table XX—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.31	1.42	1.50	2.55	2.22	1.92
10	1.35	1.55	1.43	2.48	2.28	1.74
200	1.91	2.02	2.10	2.94	2.41	2.02

Table XXI—Molecular Conductivity Rubidium Bromide in "25 per cent." Acetone.

V	15°	25°	35°	45°
2	61.2	76.6	92.6	109.7
10	63.7	79.2	95.4	111.6
50	73.3	93.8	115.4	138.4
200	75.7	96.9	119.7	143.6

Table XXII—Molecular Conductivity of Rubidium Bromide in "12.5 per cent." Acetone.

V	15°	25°	35°	45°
2	75.6	93.1	111.5	130.3
10	81.7	102.3	123.5	146.0

Table XXIII—Molecular Conductivity Rubidium Chloride in "75 per cent." Acetone.

V	15°	25°	35°	45°
4	25.5	30.4	35.5	40.9
10	32.5	43.1	50.1	
200	50.8	63.1	76.0	88.0

Table XXIV—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
4	0.490	0.502	0.548	1.92	1.65	1.55
10	1.063	0.696		3.27	1.62	
200	1.229	1.30	1.20	2.42	2.06	1.58

Table XXV—Molecular Conductivity Rubidium Chloride in "62.5 per cent." Acetone.

V	15°	25°	35°	45°
2	30.9	37.7	44.8	52.8
10	39.0	47.9	57.2	66.7
200	52.5	66.5	82.8	97.4

Table XXVI—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	0.688	0.710	0.798	2.23	1.88	1.78
10	0.891	0.922	0.955	2.28	1.93	1.67
200	1.20	1.632	1.46	4.37	2.46	1.77

Table XXVII—Molecular Conductivity Rubidium Chloride in "50 per cent." Acetone.

V	15°	25°	35°	45°
2	39.1	48.8	59.0	69.8
10	45.6	59.5	70.9	81.8
200	56.7	72.5	90.3	108.6

Table XXVIII—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	0.975	1.020	1.077	2.49	2.09	1.82
10	1.388	1.144	1.090	3.04	1.93	1.54
200	1.58	1.78	1.83	2.79	2.45	2.03

Table XXIX—Molecular Conductivity Rubidium Chloride in "37.5 per cent." Acetone.

V	15°	25°	35°	45°
2	49.3	61.5	74.8	88.9
10	54.5	69.2	84.4	101.5
200	63.0	82.6	100.1	121.3

Table XXX—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.225	1.325	1.419	2.49	2.16	1.90
10	1.473	1.526	1.708	2.71	2.21	2.03
200	1.952	1.759	2.12	3.10	2.13	2.12

Table XXXI—Molecular Conductivity Rubidium Chloride in "25 per cent." Acetone.

V	15°	25°	35°	45°
2	59.0	73.9	89.3	106.0
10	62.8	78.0	93.3	110.0
200	73.6	94.1	116.1	140.0

Table XXXII—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.495	1.541	1.668	2.54	2.08	1.87
10	1.520	1.532	1.674	2.42	1.97	1.80
200	2.041	2.201	2.39	2.77	2.34	2.06

Table XXXIII—Molecular Conductivity Rubidium Chloride in "12.5 per cent." Acetone.

V	15°	25°	35°	45°
2	74.3	91.2	109.4	127.9
10				
200	90.5	115.1	138.4	164.9

Table XXXIV—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.692	1.819	1.850	2.28	2.00	1.69
10						
200	2.46	2.33	2.65	2.72	2.02	1.91

Table XXXV—Molecular Conductivity Rubidium Nitrate in "75 per cent." Acetone.

V	15°	25°	35°	45°
4	32.8	39.4	46.4	53.7
10	40.0	48.3	56.9	65.7
50	51.3	62.5	74.1	86.2
100	55.4	67.4	80.7	93.9
200	58.8	71.6	85.3	99.5
400	61.1	74.4	89.0	104.3
800	63.7	79.0	94.2	110.6
1600	67.5	82.2	98.1	115.3

Table XXXVI—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
4	0.658	0.694	0.74	2.01	1.77	1.60
10	0.827	0.86	0.88	2.07	1.78	1.55
50	1.12	1.16	1.21	2.19	1.86	1.64
100	1.20	1.33	1.32	2.17	1.98	1.64
200	1.28	1.37	1.42	2.18	1.92	1.67
400	1.33	1.46	1.53	2.18	1.96	1.72
800	1.43	1.52	1.64	2.21	1.93	1.74
1600	1.47	1.59	1.72	2.18	1.94	1.75

Table XXXVII—Molecular Conductivity Rubidium Nitrate in "62.5 per cent." Acetone.

V	15°	25°	35°	45°
4	38.8	48.0	57.8	68.1
10	44.3	55.2	66.4	78.2
200	57.1	71.9	87.0	103.8

Table XXXVIII—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
4	0.926	0.98	1.03	2.39	2.04	1.78
10	1.09	1.13	1.18	2.47	2.05	1.77
200	1.48	1.51	1.68	2.59	2.09	1.93

Table XXXIX—Molecular Conductivity Rubidium Nitrate in "50 per cent." Acetone.

V	15°	25°	35°	45°
2	39.9	50.2	60.9	72.4
4	43.7	55.2	67.3	80.7
10	48.2	61.5	74.8	89.3
50	54.8	69.8	85.8	103.1
100	56.7	72.4	89.1	107.3
200	58.0	75.6	91.9	110.2
400	59.3	75.5	93.1	112.3
800	60.2	77.1	95.0	115.3
1600	59.2	76.2	94.0	113.9

Table XL—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.03	1.07	1.15	2.59	2.13	1.89
4	1.16	1.21	1.34	2.65	2.19	1.99
10	1.33	1.33	1.45	2.76	2.16	1.94
50	1.50	1.60	1.73	2.74	2.29	2.02
100	1.57	1.67	1.82	2.77	2.31	2.04
200	1.76	1.83	1.88	3.02	2.16	1.99
400	1.82	1.76	1.92	2.73	2.33	2.06
800	1.82	1.79	2.03	2.84	2.33	2.14
1600	1.70	1.78	1.99	2.88	2.34	2.12

Table XLI—Molecular Conductivity Rubidium Nitrate in "87.5 per cent." Acetone.

V	15°	25°	35°	45°
2	45.7	57.6	70.5	84.7
10	54.4	69.4	84.7	101.4
200	63.9	81.7	101.2	122.0

Table XLII—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.19	1.29	1.42	2.61	2.24	2.00
10	1.49	1.53	1.67	2.75	2.21	1.98
200	1.78	1.95	2.08	2.78	2.39	2.05

Table XLIII—Molecular Conductivity Rubidium Nitrate in "25 per cent." Acetone.

V	15°	25°	35°	45°
2	54.4	68.3	82.9	98.2
4	58.2	73.5	89.6	106.9
10	61.0	75.1	91.5	110.3
50	69.2	87.8	107.7	128.8
100	71.2	90.6	111.4	133.5
200	73.3	93.5	114.7	137.5
400	73.0	92.9	114.9	137.6
800	79.4	100.4	123.6	147.7
1600	73.3	92.8	114.2	136.6

Table XLIV—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.40	1.45	1.53	2.57	2.13	1.85
4	1.43	1.61	1.73	2.47	2.19	1.93
10	1.41	1.64	1.88	2.31	2.19	2.06
50	1.86	1.99	2.11	2.69	2.27	1.96
100	1.94	2.08	2.21	2.78	2.30	1.98
200	2.02	2.12	2.28	2.76	2.27	1.99
400	1.99	2.20	2.27	2.73	2.34	1.98
800	2.10	2.32	2.41	2.65	2.31	1.95
1600	1.95	2.14	2.24	2.66	2.31	1.96

Table XLV—Molecular Conductivity Rubidium Nitrate in "12.5 per cent." Acetone.

V	15°	25°	35°	45°
2	65.1	80.6	96.8	113.7
10	74.1	91.7	106.9	123.9
200	87.0	108.8	131.7	156.4

Table XLVI—Temperature Coefficients.

	Conductivity units per degree.			Per cent.		
V	15–25°	25–35°	35–45°	15–25°	25–35°	35–45°
2	1.55	1.62	1.69	2.38	2.00	1.75
10	1.76	1.51	1.71	2.37	1.65	1.60
200	2.18	2.29	2.47	2.50	2.10	1.88

Table XLVII—Specific Conductivity of Water-Acetone Mixtures (Multiplied by 10^3.)

Per. cent.	15°	25°	35°	45°
12.5	2.59	3.33	4.08	4.92
25.	2.52	3.23	4.02	3.86
37.5	0.94	1.20	1.50	1.82
50.	1.34	1.71	2.09	2.39
62.5	1.13	1.43	1.77	2.12
75.	0.73	0.90	1.08	1.28

TEMPERATURE COEFFICIENTS OF FLUIDITY.[1]

Table XLVIII—Rubidium Bromide in "75 per cent." Acetone.

V	15–25°	25–35°	35–45°
2	0.0251	0.0212	0.0189
4	.0256	.0220	.0187
10	.0244	.0225	.0200
solv.	.0257	.0229	.0201

Table XLIX—Rubidium Bromide in "62.5 per cent." Acetone.

2	0.0296	0.0263	0.0228
10	.0304	.0267	.0237
solv.	.0309	.0272	.0245

Table L—Rubidium Bromide in "50 per cent." Acetone.

V	15–25°	25–35°	35–45°
1	0.0316	0.0270	0.0234
4/3	.0311		
2	.0314	.0275	.0244
4	.0333	.0281	.0229
10	.0333	.0281	.0268
solv.	.0315	.0284	.0262

Table LI—Rubidium Bromide in "25 per cent." Acetone.

2	0.0337	0.0294	0.0257
10	.0347	.0304	.0261
solv.	.0343	.0297	.0267

Table LII—Rubidium Bromide in "12.5 per cent." Acetone.

V	15–25°	25–35°	35–45°
2	0.0307	0.0276	0.0238
4	.0337	.0287	.0243
10	.0330	.0291	.0256
solv.	.0338	.0299	.0250

[1] Davis, Hughes and Jones, Zeit. f. phys. Chem. (1913).

Discussion.

The investigation of the conductivity of solutions of rubidium salts has been carried out in parallel with work on the viscosity of these solutions, and will be discussed in its relation to that side of the problem. The conductivities of solutions of rubidium iodide, bromide, chloride, and nitrate in mixtures of ace-

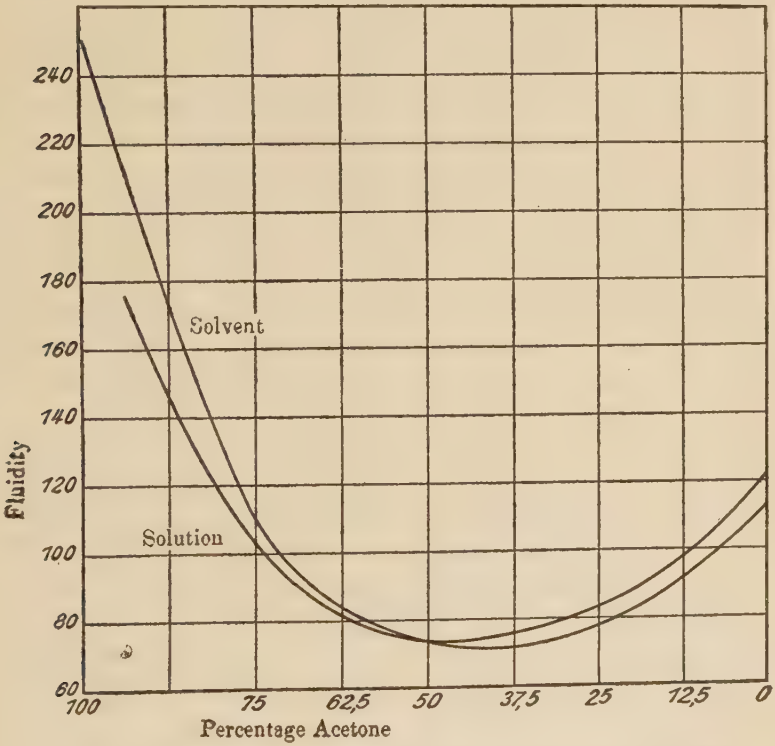

Fig. 1—Fluidity of Rubidium Iodide Solution and Solvent.

tone and water, have been measured in the dilutions indicated in the tables and are compared with the viscosities of dilutions up to the tenth normal: the viscosities of dilutions greater than tenth normal do not differ sufficiently from that of the solvent

to give data of any significance. It was not possible to obtain satisfactory solutions of these salts in pure acetone on account of their slight solubility in this solvent. Their great solubility in water made it possible to obtain quite concentrated solutions

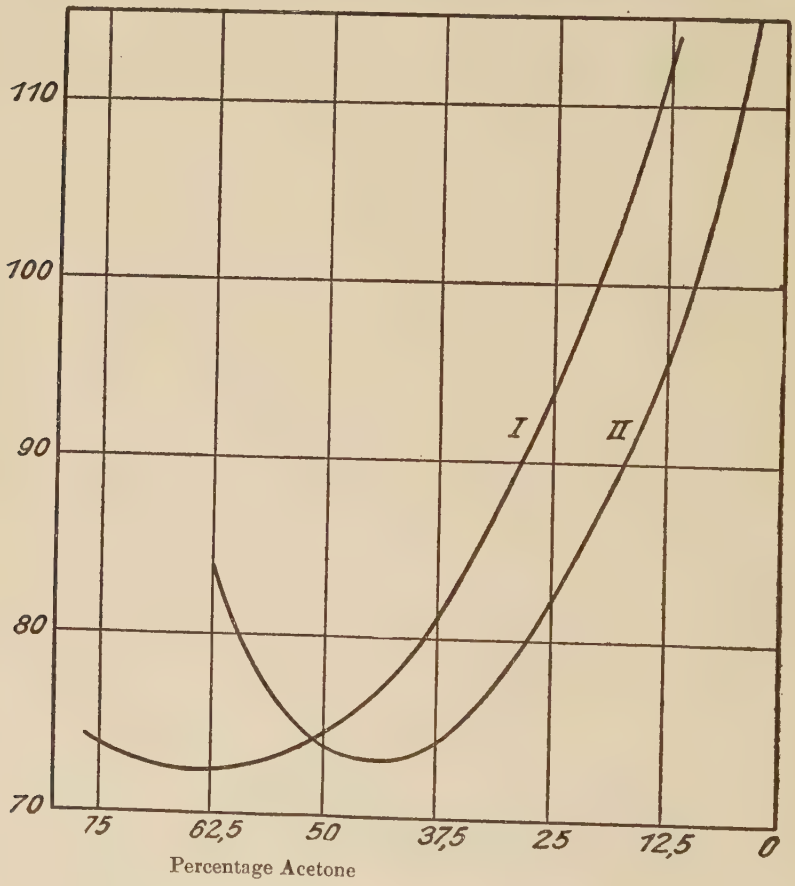

FIG. 2—CONDUCTIVITY AND VISCOSITY OF RUBIDIUM BROMIDE.
CURVE I, ORDINATES: MOLECULAR CONDUCTIVITY;
CURVE II, ORDINATES: FLUIDITY.

in the majority of mixed solvents, even in that containing ninety per cent. acetone. One exception was noted: the attempt

to prepare a N/2 solution of rubidium chloride in "75 per cent." acetone resulted in obtaining a solution which was non-miscible with the solvent at 20°, though at 15°, a homogeneous solution was obtained.

It was found by Jones and Veazey,[1] that the curves expressing the fluidity of varying mixtures of acetone and water are almost exactly parallel to those for the conductivity of potassium sulphocyanate in solution in the same mixtures. (The conductivity curve of *KSCN* is parallel to Curve II, Fig. 2.) The fluidity curve for acetone has a minimum between 37.5 per cent. and 50 per cent.; and the fluidity for the rubidium halides and nitrate has its minimum in approximately the same position, Fig. 1. The conductivity curves, however, of the rubidium salts have their minima corresponding to a much greater percentage of acetone, Fig. 2. As has been shown by previous workers, this minimum in fluidity occurs at the position where the breaking down of the association of one solvent by the other is greatest. The conductivity depends upon the velocities of the ions and the degree of dissociation. The dissociation is least when the association of the solvent is least, and the speed of the ions is least when the fluidity is least. Therefore, if these were the only determining factors, the conductivity minima would always correspond to the fluidity minima.

Potassium sulphocyanate has a considerable solubility in pure acetone (about 20 grams in 100 grams of acetone at 20°), whereas the rubidium salts studied are only slightly soluble in pure acetone. Therefore, in the same concentrations, the rubidium salts are nearer saturation than potassium sulphocyanate. The percentage dissociation is, therefore, lower in the case of rubidium salts than in that of potassium sulphocyanate. A possible explanation of the shifting of the minimum in the conductivity of rubidium salts, towards the greater proportions of acetone, is that the great insolubility in acetone might cause the dissociation to be driven back. This shifting of the mini-

[1] Amer. Chem. Jour. 37, 405 (1907).

mum by the slight solubility, however, seems to be clearly manifested only between salts with great difference in solubility in acetone; as is the case of potassium sulphocyanate and the rubidium halides.

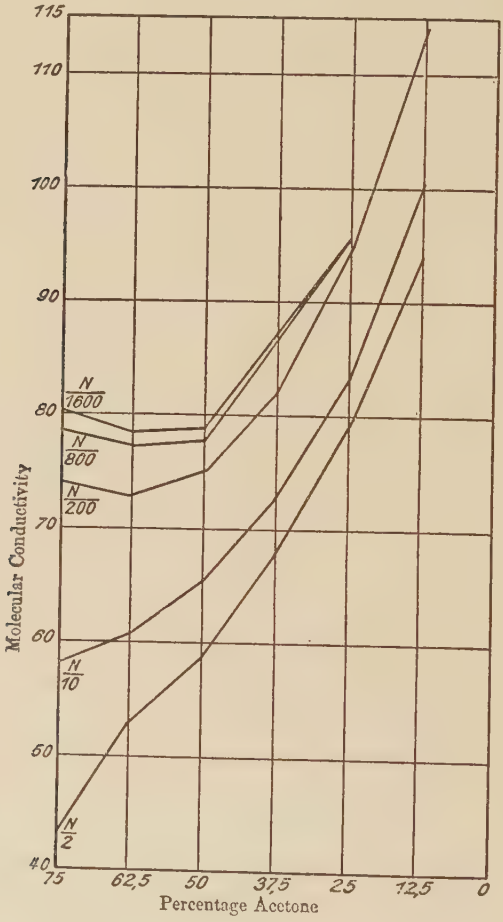

Fig. 3—Conductivity of Rubidium Iodide.

Of the four salts, rubidium chloride, iodide, bromide, and nitrate, the solubility in acetone of the iodide only is accurately

known; so that these salts could not be compared with each other for the relation between solubility and minimum conductivity.

The relative solubilities in water probably do not correspond

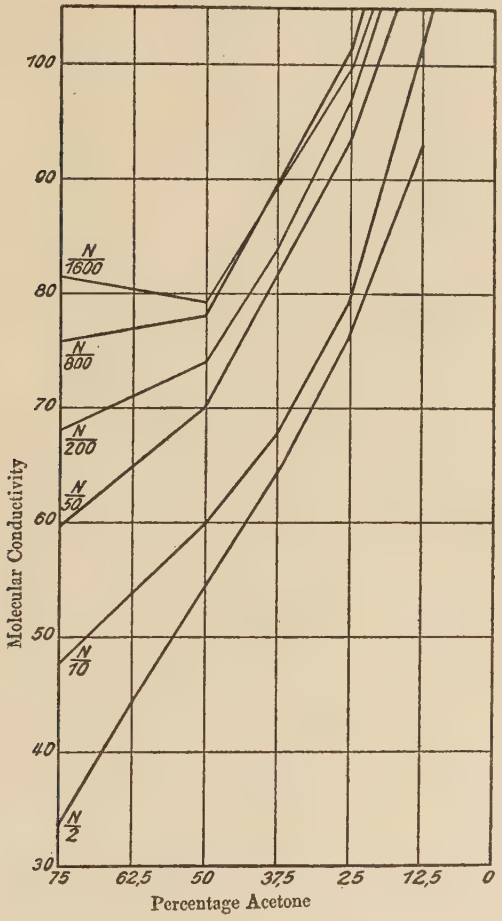

Fig. 4—Conductivity of Rubidium Bromide.

to the relative solubilities in acetone. The iodide and the nitrate are, respectively, the most soluble and the least soluble in water; but the conductivity minima of these two salts are

the farthest from the ordinate corresponding to one hundred per cent. acetone. (Figs. 3-6.)

It is not to be expected that the differences in solubility in water of the different rubidium salts would show this relation,

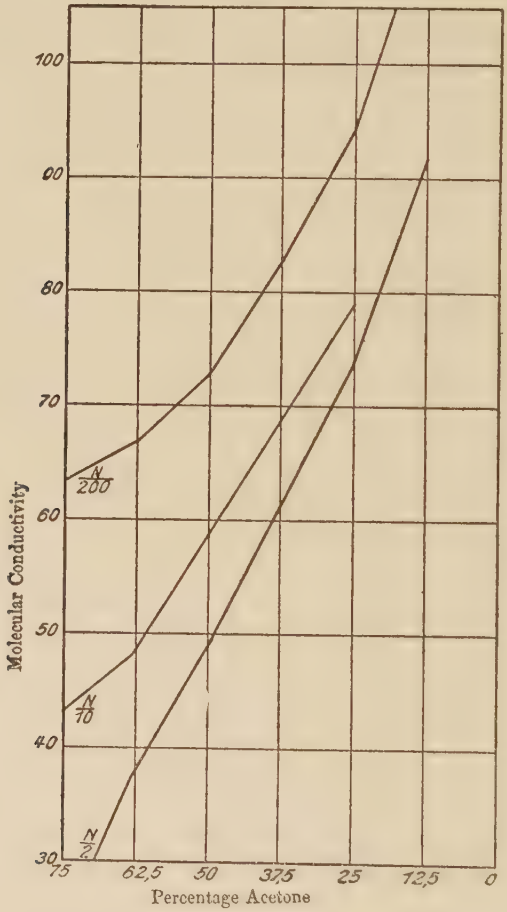

FIG. 5—CONDUCTIVITY OF RUBIDIUM CHLORIDE.

because in the dilutions which are sufficiently great to give any minimum at all, these salts are very far from their saturation in water. In the dilutions greater than N/800, that is, where

the dissociation approaches completeness, the minima in the conductivity curves are seen to be nearer those of fluidity, (Figs. 3 and 6).

A comparison of the percentage coefficients of fluidity with

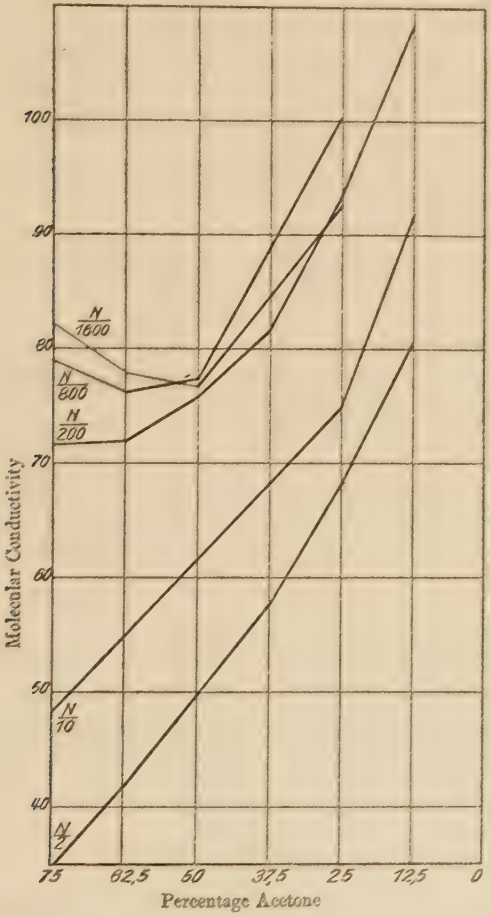

Fig. 6—Conductivity of Rubidium Nitrate.

those of conductivity, shows that the two are nearly equal, which is to be expected in the case of a non-solvated salt. For the same salt the coefficients for conductivity, while nearly equal,

are somewhat smaller than those for fluidity. As Davis and Jones have pointed out, this is due to "the decrease in association of the solvent with rise in temperature, causing a decrease in the ionization of the solute, and therefore a smaller conductivity."

In most cases the molecular conductivities of N/800 and N/1600 are practically the same, showing that the dissociation has apparently become constant. If the conductivity depends only upon the velocity of the ions and the number of ions present, then, in the case of a non-hydrated electrolyte, since velocity is proportional to fluidity,

$$\frac{\mu_\infty \text{ in solvent}}{\mu_\infty \text{ in water}} = \frac{\phi \text{ of solvent}}{\phi \text{ of water}}$$

This would indicate a value of $\mu_\infty = 102.$ for rubidium bromide at 25° in "50 per cent." acetone. The molecular conductivity becomes constant at about 80.

This indicates either that the equilibrium between ions and molecules becomes constant at $\alpha = 80/102 = 78$ per cent. (where α is the percentage dissociation); or that the dissociation is complete at the N/800 dilution, and the molecular conductivity is decreased by a decreasing velocity of the ions. The first cause seems improbable. The second may seem unlikely in view of the fact that at high concentrations, rubidium salts are not appreciably solvated. This, however, is not evidence that there is no solvation at great dilution. And this would seem to be the most probable explanation of the low constant value for μ.

Summary.

1. Minima in the conductivity curves for rubidium salts correspond to a higher percentage of acetone in the solvent mixtures that do those in the fluidity curves, while the two curves are parallel for certain other salts. A possible explanation based on the difference in solubility is offered.

2. A comparison of the temperature coefficients of conductivity and fluidity shows that these are what is to be expected in the case of a non-solvated salt in a mixture of associated solvents.

3. Rubidium salts increase the viscosity of all mixtures containing more than "50 per cent." acetone.

4. A possible indication of solvation of rubidium salts in dilute solutions is pointed out.

Biography.

The author of this dissertation was born in Charleston, South Carolina, October 20, 1885. He received the degree of Bachelor of Science from the College of Charleston in 1905, and that of Master of Arts in 1906. In November, 1911, he entered the Johns Hopkins University as a graduate student in Chemistry. His subordinate studies were Physical Chemistry and Geology.